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(54) **Non-hairing moisture curable compositions.**

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Description

This invention relates to polyurethane hot melt compositions. Such compositions are useful as adhesives, coatings and sealants for example.

Polyurethane compositions are desirable in a variety of applications because of their excellent properties. They can be one-part and two-part solvent-borne systems, water-based systems or 100%-reactive solvent-free adhesive systems. Of particular utility are the reactive hot melt urethane adhesive systems which combine the rapid set or crystallization times of conventional hot melt adhesives with the high bond strengths of a curing system. Like conventional hot melts, the reactive hot melt urethane adhesives are solid at room temperature, melt to a viscous liquid when heated to moderate temperatures (82-121 °C), and are applied in the molten state. The adhesive then cools to a solid state to provide initial bond strength (i.e., green strength) and additionally, cures on contact with ambient moisture to provide its final bond strength. These urethane-based systems are superior to conventional hot melt adhesives which lack resistance to solvents and heat, have lower bond strengths, and which can creep under load because they are non-curing.

In general, hot melt systems, including the urethane-based systems, suffer from the disadvantage of "stringing" or "hairing" during application at dispensing temperatures, especially in automated dispensing equipment. By stringing or hairing is meant that during application by extrusion, thin threads of the molten system form at the applicator tip when it is removed from the point where the hot melt adhesive has been deposited. Hairing is undesirable in many applications such as electronic assembly, because of the contamination it introduces. Additionally, hairing can contaminate the work station and application equipment.

The present invention overcomes this problem by providing a moisture curable, non-hairing hot melt composition of simple formulation. In certain embodiments, the composition also exhibits improved crystallization rates and possesses high green strength.

Chemical Abstracts <u>108</u>:23061h (1988) discloses polyurethane adhesives composed of one or more polyester diols of MW 700 to 2500 having 2 to 4 methylene groups per diol and another polyesterdiol of MW 1000 to 3500 having 5 to 10 methylene groups per diol which are reacted with a diisocyanate. One such adhesive specifically disclosed is made from 25 parts poly(1,6-hexylene adipate)diol (MW = 2600) 75 parts poly(ethylene 1,4-butylene adipate)diol (MW = 1000) and 20.6 parts xylylene diisocyanate.

In accordance with the present invention there is provided a non-hairing, moisture curable hot melt composition having a number average molecular weight between 1,000 and 10,000 comprising the reaction product of two or more hydroxy-functional polymers with polyisocyanates wherein said hydroxy functional polymers are selected from:

(1) linear polyester blends comprising a first and second polyester, wherein each polyester is the reaction product of a polyol and a polyacid,
wherein

$$a + b < \text{or} = 4,\ c + d > \text{or} = 6$$
$$a + b > 4 \text{ and} \leq 6,\ c + d > \text{or} = 10$$
$$a + b > 6 \text{ and} \leq 8,\ c + d > \text{or} = 12$$

wherein a is the number of methylene moieties in the polyol used to form the first polyester,
b is the number of methylene moieties in the polyacid used to form the first polyester,
c is the number of methylene moieties in the polyol used to form the second polyester of the blend, d is the number of methylene moieties in the polyacid used to form the second polyester of the blend; and

(2) a blend of at least one non-linear polyester and one linear polyester, wherein the non-linear polyester is selected from polyneopentyl adipate, polypropylene adipate and polycyclohexanedimethyl adipate, and the linear polyester is selected from polyethylene adipate, polybutylene succinate, and polyhexamethylene sebacate, provided that when the linear polyester is polyhexamethylene sebacate, the non-linear polyester is polyneopentyl adipate or polypropylene adipate; and

(3) a blend of poly ϵ-caprolactone and at least one linear polyester selected from polyethylene adipate, polyethylene succinate and polybutylene succinate.

The isocyanate-terminated mixture preferably has a number average molecular weight of 1,000 to 6,000, and most preferably of 3,000 to 4,500. Additionally, the mixture preferably forms an essentially non phasing blend at application temperature (about 100 °C). By essentially non phasing is meant that, on visual inspection of the melt, there is no gross separation of the hydroxy functional polymers after extended (e.g. 1 hr.) heating at 100 °C.

The invention also provides a method for bonding substrates which comprises contacting a substrate with a bond-forming amount of a hot melt moisture curable composition in accordance with the present invention.

There is also provided a mixture of hydroxy functional polymers comprising

(1) linear polyester blends, comprising a first and second polyester wherein each polyester is the reaction product of a polyol and a polyacid,

wherein

$$a + b < \text{or} = 4, c + d > \text{or} = 6$$
$$a + b > 4 \text{ and} \leq 6, c + d > \text{or} = 10$$
$$a + b > 6 \text{ and} \leq 8, c + d > \text{or} = 12$$

wherein a is the number of methylene moieties in the polyol used to form the first polyester, b is the number of methylene moieties in the polyacid used to form the first polyester, c is the number of methylene moieties in the polyol used to form the second polyester of the blend, d is the number of methylene moieties in the polyacid used to form the second polyester of the blend; and

(2) a blend of at least one non-linear polyester and one linear polyester, wherein the non-linear polyester is selected from polyneopentyl adipate, polypropylene adipate and polycyclohexanedimethyl adipate, and the linear polyester is selected from polyethylene adipate, polybutylene succinate, and polyhexamethylene sebacate, provided that when the linear polyester is polyhexamethylene sebacate, the non-linear polyester is polyneopentyl adipate or polypropylene adipate; and

(3) a blend of poly ϵ-caprolactone and at least one linear polyester selected from polyethylene adipate, polyethylene succinate and polybutylene succinate.

There is also provided a blend of hydroxy-functional polymers comprising

(1) linear polyester blends, wherein the polyester is the reaction product of a diol and a diacid, wherein

$$a + b = 4, c + d > \text{or} = 6$$
$$a + b = 6, c + d > \text{or} = 10$$
$$a + b = 8, c + d > \text{or} = 12$$

wherein a is the number of methylene moieties in the diol used to form the first polyester, b is the number of methylene moieties in the diacid used to form the first polyester, c is the number of methylene moieties in the dial used to form the second polyester, d is the number of methylene moieties in tee diacid used to form the second polyester; and

(2) a blend of a linear and a non-linear polyester, wherein the non-linear polyester is selected from polyneopentyl adipate, polypropylene adipate and polycyclohexanedimethyl adipate, and the linear polyester is selected from polyethylene adipate, polybutylene succinate, and polyhexamethylene sebacate, provided that when the linear polyester is polyhexamethylene sebacate, the non-linear polyester is polyneopentyl adipate or polypropylene adipate;

(3) a mixture of polyethylene adipate and polyhexamethylene adipate; or

(4) a mixture of linear polyesters wherein one of the liner polyesters is poly ϵ-caprolactone and the others are selected from polyethylene adipate, polyethylene succinate and polybutylene succinate.

The preparation of isocyanate-terminated prepolymers is well known in the art. Suitable prepolymers with residual isocyanate groups are formed by reaction of (1) a mixture of two or more hydroxy functional polymers as defined above wherein the total mixture generally has a combined number average molecular weight of 1,000 to 10,000, preferably of 1,000 to 6,000, and more preferably of 3,000 to 4,500 and (2) a polyisocyanate, preferably a diisocyanate.

The prepolymer is preferably at least partially comprised of crystalline or semicrystalline polyester diols. Preferred polyesters have melting points between 30 °C and 80 °C, most preferred between 40 °C and 60 °C. Amorphous polyesters with glass transition temperatures up to 50 °C may be useful in blends at less than 50% total polyester weight. In certain cases liquid polyesters may be useful in blends of polyesters at less than 30% total polyester weight. Such preferred polyesters can be prepared by reacting a diol with a diacid or derivatives of diacids. Especially preferred are polyesters prepared by reacting short chain diols having the structure

$HO\text{-}(CH_2)_x\text{-}OH$, where x is from 2 to 8, with diacids having the structure $HOOC\text{-}(CH_2)_y\text{-}COOH$, where y is from 1 to 10. Examples of useful diols include ethylene glycol, 1,4-butanediol, 1,6-hexanediol; 1,4-cyclohexane dimethanol, neopentyl glycol and 1,2-propylene glycol. Examples of useful diacids include adipic, azelaic, succinic, and sebacic acids. Small amounts of triols, polyethers and up to 30 mole percent

of other diacids and anhydrides such as isophthalic, terephthalic, cyclohexane dicarboxylic acid and phthalic anhydride may also be useful in the preferred polyester synthesis.

Examples of commerically available polyesters that are useful in the compositions of the invention are the "Lexorez" (Registered Trade Mark) series commerically available from Inolex Chemical Co. Specific examples of such resins include Lexorez 1130-30P, Lexorez 1150-30P, and Lexorez 1110-25P. Examples of other commercially available polyesters useful in the invention are the "Rucoflex" (Registered Trade Mark) series of resins available from Ruco Polymer Corporation.

An example of a commerically available polylactone that is useful in the invention is "Tone-0260" (Registered Trade Mark), commercially available from Union Carbide. Component ratios can be determined by the performance properties desired.

Particularly preferred mixtures of hydroxy functional polymers are:

(1) linear polyester blends, wherein the polyester is the reaction product of a diol and a diacid, wherein

$$a + b = 4, c + d > \text{or} = 6$$
$$a + b = 6, c + d > \text{or} = 10$$
$$a + b = 8, c + d > \text{or} = 12$$

wherein a, b, c, and d are as described above.

(2) a blend of a linear and non linear polyesters, wherein the non linear polyester is selected from the group consisting of polyneopentyl adipate, polypropylene adipate and polycyclohexanedimethyl adipate, and the linear polyester is selected from the group consisting of polyethylene adipate, polybutylene succinate, and polyhexamethylene sebacate provided that when the linear polyester is polyhexamethylene sebacate, the non-linear polyester is polyneopentyl adipate or polypropylene adipate;

(3) a mixture of polyethylene adipate and polyhexamethylene adipate; or

(4) a mixture of linear polyesters wherein one of the linear polyesters is poly ϵ-caprolactone and the others are selected from the group consisting of polyethylene adipate, polyethylene succinate and polybutylene succinate.

The ratio of polyesters employed in the invention can vary in the composition. However, it has been found preferable to employ a weight ratio of first to second polyesters in the range of between about 85:15 to 15:85, more preferably 80:20 to 20:80, most preferably 70:30 to 30:70.

The polyisocyanates which are reacted with the hydroxy functional polymers to form the prepolymers used in the instant invention can be aliphatic or aromatic. Preferably they are aromatic diisocyanates such as diphenylmethane-2,4'-diisocyanate and/or 4,4'-diisocyanate; tolylene-2,4-diisocyanate and -2,6-diisocyanate and mixtures thereof. Other examples include: naphthylene-1,5-diisocyanate; triphenylmethane-4,4'4"-triisocyanate; phenylene-1,3-diisocyanate and -1,4-diisocyanate; dimethyl-3,3'-biphenylene-4,4'-diisocyanate; diphenylisopropylidine-4,4'-diisocyanate; biphenylene diisocyanate; xylylene-1,3-diisocyanate and xylylene -1,4-diisocyanate.

A list of useful commercially available polyisocyanates is found in the Encyclopedia of Chemical Technology, Kirk-Othmer, 2nd Ed., Vol. 12, pp. 46-47, Interscience Pub., N.Y. (1967), which list is incorporated herein by reference. Especially preferable isocyanates include diphenylmethane-4,4'-diisocyanate (MDI) and tolylene-2,4-diisocyanate/tolylene-2,6-diisocyanate (TDI) and mixtures thereof.

Isocyanate-functional derivative(s) of MDI and TDI may be used, such as liquid mixtures of the isocyanate-functional derivative with melting point modifiers (e.g., mixtures of MDI with polycarbodiimide adducts such as "Isonate 143L" (Registered Trade Mark), commercially available from the Dow Chemical Co., and "Mondur CD" (Registered Trade Mark), commercially available from Mobay Chemical Corp.; small amounts of polymeric diphenylmethane diisocyanates, preferably 10% or less by weight of the total isocyanate component, (e.g., "PAPI", and the series "PAPI 20" through "PAPI 901" (Registered Trade Marks), commercially available from the Dow Chemical Co., "Mondur MR", "Mondur MRS", and "Mondur MRS-10" (Registered Trade Marks), commercially available from Mobay Chemical Corp., and "Rubinate M" (Registered Trade Mark)", commercially available from ICI Chemicals, Inc.); and blocked isocyanate compounds formed by reacting aromatic isocyanates or the above-described isocyanate-functional derivatives with blocking agents such as ketoximes. Such blocked isocyanate-functional derivatives, will for convenience, be regarded herein as isocyanate-functional derivatives of MDI and TDI.

The isocyanate should preferably be present in the prepolymer composition in an equivalent amount greater than that of the hydroxy containing component. The equivalent ratio of isocyanate to hydroxyl is preferably from about 1.2 to about 10 to 1.0 and especially preferably from about 1.6 to 2.2 to 1.0.

The compositions of the invention can optionally contain other ingredients or adjuvants if desired. For example, chain extension agents (e.g., short chain polyols such as ethylene glycol or butanediol) fillers (e.g.

carbon black, metal oxides such as zinc oxide, and minerals such as talc, clays, silica, silicates), thermoplastic resins, plasticizers, antioxidants, pigments, U.V. absorbers, adhesion promoters such as silanes may be included to impart particular characteristics to the composition. They should be added only to the levels that do not interfere with the non-hairing characteristic of the composition. These adjuvants generally comprise up to 50 weight percent of the composition either individually or in combination.

In addition, the compositions can optionally contain an effective amount of catalyst or reaction accelerator such as tertiary amines, metal-organic compounds, co-curatives such as oxazolidine. Dibutyltin dilaurate is a preferred metal organic catalyst. An effective amount of metal-organic catalyst is preferably from about 0.01 to 2 percent by weight of the prepolymer. More preferably, the catalyst is present at a level of about 0.05 to about 1 percent, based on the weight of the prepolymer.

The adhesive compositions of the invention may be prepared by mixing the components at elevated temperature, using conventional mixing techniques. It is preferred to mix the components under anhydrous conditions. Generally, preparation of the adhesive is done without the use of solvents.

The hot melt compositions of the invention achieve their initial, or green, strength through crystallization, then continue to cure by exposure to water, e.g., water vapor or moisture. High humidity and heat will provide an accelerated rate of cure while low humidity (e.g., 15% R.H. or less) will provide a slower rate of cure.

While the composition of the invention is preferably essentially non-phasing, some separation of the polyester components is acceptable. Moreover, the degree of phasing can be adjusted by varying any or several of certain factors. For example, the degree of chain extension of the polyester, the molecular weight of the polyester and the choice of isocyanate all influence phase separation. For example, as the molecular weight of the polyester decreases, the compatability of the blend increases. Additionally, as the NCO|OH ratio decreases the compatability of the components in the prepolymer increases. Moreover, simply varying the ratios of the polyester components influences their compatability as shown herein.

The compositions of the invention can be employed in any application where a high-performance adhesive, coating, or sealant is desired. They can be applied to a variety of articles and substrates, such as thermoplastic materials, thermosetting materials, foam material, wood, paper, leather, rubber, textiles, non-woven materials and bare and painted metals.

The following examples are offered to aid understanding of the present invention and are not to be construed as limiting the scope thereof. All parts are by weight unless otherwise stated.

Examples 1-7

Preparation and testing of isocyanate-terminated hydroxy functional polymer compositions.

In a 600 ml, stainless steel reactor with a gas inlet adapter and fitted with a cover having a rubber gasket, gas inlet and stirrer opening, the hydroxy functional polymer or mixture of polymers was heated to 100°C with efficient stirring and nitrogen blanket. 4,4'-Diphenylmethane diisocyanate was added with stirring. The mixture was stirred under nitrogen for about 15 minutes and dibutyltin dilaurate (DBTDL) was added. Stirring was continued under vacuum for about 1 hour. Heating at 100°C was maintained throughout. The resulting mixture was poured into nitrogen purged metal containers and sealed. The containers were stored in a dessicator.

Viscosity determinations were made using a Brookfield RVF Viscometer and #27 spindle at 121°C at 10 rpm or 20 rpm. Number average molecular weights (Mn) were determined by end group analysis.

The non-hairing property was determined by visual observation. If there were no strings or hairs trailing from a hot melt applicator nozzle, the composition was deemed non-hairing.

Table 1

Polyol, OH eq.	Ex. 1	Ex. 2*	Ex. 3*	Ex. 4*	Ex. 5*	Ex. 6*	Ex. 7*
PHA(1)	.55	.55		1			
PEA(2)	.45		.45		1		
PBA(3)		.45	.55			1	
MDI NCO EQ	2	2	2	2	2	2	2
DBTDL(wgt. %)	.1	.1	.1	.1	.1	.1	.1
Visc.(Cps)	12825	6550	10850	6150	5812	19375	6250
Non-hair	yes	no	no	no	no	no	no

(1) 1,6-Polyhexamethylene adipate, Hydroxyl No. 30 mg KOH/g sample, Mn 3741
(2) Polyethylene adipate, Hydroxyl No. 25 mg KOH/g sample, Mn 4489
(3) 1,4-Polybutylene adipate, Hydroxyl No. 30 mg KOH/g sample, Mn 3741
* Comparative

These Examples show that only compositions according to the invention are non-hairing.

Examples 8-9

The procedure and tests of Examples 1-7 was repeated. The results are given in Table 2.

Table 2

Polyol OH eq.	Ex. 8	Ex. 9*
PEA	.45	
PBA		.45
PCP(1)	.55	.55
MDI NCO EQ	2	2
DBTDL(wgt. %)	.1	.1
Visc. (Cps)	10088	13875
Non-hair	yes	no

(1) Poly ϵ-Caprolactone, Hydroxyl No. 37 mg KOH/g sample, Mn 3033
* Comparative

Examples 10-16

The following examples show the correlation between isocyanate-terminated polymer mixtures and polymer mixtures not reacted with isocyanate. The polymer mixtures are not reacted with the isocyanate for ease of handling.

Blends were prepared by manually stirring the components at a temperature of about 120 °C until well mixed, which was about 10 minutes. The presence or absence of hairing was determined by a visual inspection by observing if "hairs" of liquid adhesive form when a spatula contacting the surface of a melted sample was removed from that surface. If there were no "hairs", the composition was deemed to be non-hairing. This method correlates to application out of a hot melt applicator.

Table 3

Example No.	Parts PHA	Parts PEA	Parts PBA	Parts PCP	Non-Hairing
10	50	50			yes
11*	50		50		no
12*		50	50		no
13		50		50	yes
14*			50	50	no
15*	100				no
16*		100			no

* Comparative

A comparison of the results in Tables 1, 2 and 3 show that the results obtained with the isocyanate-reacted hydroxy functional polymers and the hydroxy functional polymers which were not reacted with the isocyanate are the same.

Examples 17-23

Using the same procedures as those in Examples 10-16, several blends of varying molecular weight are prepared and evaluated. Set out in the table below are the formulations and hairing property determination.

Table 4

Ex. No.	PHA	PEA-25(1)	PEA-55(2)	PEA-110(3)	Non-Hairing
17*	100				no
18*		100			no
19*			100		no
20 *				100	no
21	50	50			yes
22	50		50		yes
23*	50			50	no

* Comparative
(1) Polyethylene adipate, Hydroxyl No. 25 mg KOH/g sample, Mn 4489
(2) Polyethylene adipate, Hydroxyl No. 55 mg KOH/g sample, Mn 2040
(3) Polyethylene adipate, Hydroxyl No.110 mg KCH/g sample, Mn 1020

An analysis of these results show that the substitution of a component with its lower molecular weight analog affects the non-hairing characteristic of the composition.

Examples 24-37

Examples 24-37 illustrate the effect of varying the ratio of the amount of individual polyesters in the mixture. The blends were prepared using the same technique as in Examples 10-16. The results are shown in Table 5.

Table 5

Ex. No.	Parts of PHA	Parts of PEA	Non-Hairing
24*	100		no
25*		100	no
26*	95	5	no
27*	90	10	no
28*	85	15	no
29	80	20	borderline
30	75	25	yes
31	70	30	yes
32	50	50	yes
33	25	75	yes
34	20	80	borderline
35*	15	85	no
36*	10	90	no
37*	5	95	no

* Comparative

The results show that the ratio of components in the blend influences the non-hairing property.

Examples 38-82

Blends of polyesters in a 1:1 ratio by weight were prepared and tested for non-hairing using the following test method:

The 0.20 cm diameter end of a 14.6 cm long wooden dowel contacted the surface of a sample whose temperature was 121 °C and was drawn away from that surface using an electric motor at a speed of 12 cm/second over a distance of 10.2 cm. If the adhesive "trail" from the dowel end was less than 7.6 cm long as it was being removed from the sample surface, the sample was deemed non-hairing. If it was more than 7.6 cm long, the sample was deemed to be hairing.

Results are set out in Table 6 below. For simplicity the following abbreviations are used:
a is the number of $-CH_2-$ groups in the diol used to form the first polyester,
b is the number of $-CH_2-$ groups in the diacid used to form the first polyester,
c is the number of $-CH_2-$ groups in the diol used to form the second polyester,
d is the number of $-CH_2-$ groups in the diacid used to form the second polyester.
PESu = polyethylene succinate, Mn 3740
PEA = polyethylene adipate, Mn 4489
PESe = polyethylene sebacate, Mn 4172
PBSu = 1,4-polybutylene succinate, Mn 5318
PBA = 1,4-polybutylene adipate, Mn 3741
PBSe = 1,4-polybutylene sebacate, Mn 3856
PBAz = 1,4-polybutylene azelate, Mn 3704
PHSu = 1,6-polyhexamethylene succinate, Mn 3591
PHA = 1,6-polyhexamethylene adipate, Mn 3741
PHSe = 1,6-polyhexamethylene sebacate, Mn 4922

Table 6

Ex. No.	Polyester I (a+b)		Polyester II (c+d)		Non-Hairing
38	PESu	(4)	PEA	(6)	yes
39	PESu	(4)	PESe	(10)	yes
40	PESu	(4)	PBSu	(6)	yes
41	PESu	(4)	PBA	(8)	yes
42	PESu	(4)	PBSe	(12)	yes
43	PESu	(4)	PHSu	(8)	yes
44	PESu	(4)	PHA	(10)	yes
45	PESu	(4)	PHSe	(14)	yes
46	PEA	(6)	PESe	(10)	yes
47*	PEA	(6)	PBSu	(6)	no
48*	PEA	(6)	PBA	(8)	no
49	PEA	(6)	PBSe	(12)	yes
50*	PEA	(6)	PHSu	(8)	no
51	PEA	(6)	PHA	(10)	yes
52	PEA	(6)	PHSe	(14)	yes
53	PBSu	(6)	PESe	(10)	yes
54*	PBA	(8)	PESe	(10)	no
55*	PESe	(10)	PBSe	(12)	no
56*	PHSu	(8)	PESe	(10)	no
57*	PESe	(10)	PHA	(10)	no
58*	PESe	(10)	PHSe	(14)	no
59*	PBSu	(6)	PBA	(8)	no
60	PBSu	(6)	PBSe	(12)	yes
61*	PBSu	(6)	PHSu	(8)	no
62	PBSu	(6)	PHA	(10)	yes
63	PBSu	(6)	PHSe	(14)	yes
64	PBA	(8)	PBSe	(12)	yes
65*	PBA	(8)	PHSu	(8)	no
66*	PBA	(8)	PHA	(10)	no
67	PBA	(8)	PHSe	(14)	yes
68	PHSu	(8)	PBSe	(12)	yes
69*	PHA	(10)	PBSe	(12)	no
70*	PBSe	(12)	PHSe	(14)	no
71*	PHSu	(8)	PHA	(10)	no

Table 6 - continued

Ex. No.	Polyester I (a+b)		Polyester II (c+d)		Non-Hairing
72	PHSu	(8)	PHSe	(14)	yes
73*	PHA	(10)	PHSe	(14)	no
74	PESu	(4)	PBAz	(11)	yes
75	PEA	(6)	PBAz	(11)	yes
76*	PESe	(10)	PBAz	(11)	no
77	PBSu	(6)	PBAz	(11)	yes
78*	PBA	(8)	PBAz	(11)	no
79*	PBAz	(11)	PBSe	(12)	no
80*	PHSu	(8)	PBAz	(11)	no
81*	PHA	(10)	PBAz	(11)	no
82*	PBAz	(11)	PHSe	(14)	no

* Comparative

These examples illustrate that the linear polyester blends useful in the compositions of the invention follow the general formula

a + b < or = 4, c + d > or = 6
a + b > 4 and,≤ 6, c + d > or = 10
a + b > 6 and ≤ 8, c + d > or = 12

and that most preferably

a + b = 4, c + d > or = 6
a + b = 6, c + d > or = 10
a + b = 8, c + d > or = 12

Examples 83-109

The following examples were prepared and tested as in Examples 38-82 using non-linear polyesters as one polyester component.

Polyester blends (1:1 ratio) and their non-hairing properties are set out in Table 7 below, where in addition to the abbreviations used in examples 38-82, the following abbreviations are used.
PNA = polyneopentyl adipate, Mn 2953
CHDMA = 1,4-polycyclohexanedimethyl adipate, Mn 3262
PCP = poly ϵ-caprolactone, Mn 3033
PPA = 1,2-polypropylene adipate, Mn 2373

Table 7

Ex. No.	Polyester I	Polyester II	Non-Hairing
83	PNA	PEA	yes
84*	PNA	PESe	no
85	PNA	PBSu	yes
86*	PNA	PBA	no
87*	PNA	PBAz	no
88*	PNA	PHA	no
89	PNA	PHSe	yes
90	CHDMA	PEA	yes
91*	CHDMA	PBA	no
92*	CHDMA	PBA	no
93	CHDMA	PBSu	yes
94*	CHDMA	PHSe	no
95	PCP	PESu	yes
96*	PCP	PESe	no
97	PCP	PBSu	yes
98*	PCP	PBAz	no
99*	PCP	PBSe	no
100*	PCP	PHSu	no
101	PPA	PESu	yes
102*	PPA	PEA	no
103*	PPA	PESe	no
104*	PPA	PBSu	no
105*	PPA	PBA	no
106*	PPA	PBAz	no
107	PPA	PBSe	yes
108*	PPA	PHSu	no
109	PPA	PHSe	yes

* Comparative

These examples illustrate useful combinations of non-linear and linear polyesters in the compositions of the invention that show the desired non-hairing property.

Examples 110-113

The following examples show the effect of the degree of phase separation (or incompatibility) on the green strength build-up of isocyanate-terminated hydroxy functional polymer compositions.

Blends were prepared as in Examples 1-7. In addition to the viscosity and non-hairing (determined as in Examples 1-7) measurements, the blends were tested for degree of phase separation and ability to hold a sustained load.

Phase separation was determined as follows:

Approximately one gram of molten polymer blend was placed on a microscope slide and the melt was drawn out into a 0.1 to 0.2 mm thick film. The slide was then placed in a 100 °C. oven for 60 minutes, then removed from the oven, allowed to cool undisturbed at room temperature and the film was visibly inspected for the formation of circular and elongated domains. The percent of the total melt area occupied by these domains was recorded as the percent of phase separation.

Green strength build-up was determined as follows:

A 0.5 ± 0.05 g quantity of adhesive was extruded at 107 °C. onto the center portion (about 5 cm from each end) of a 2.5 cm wide x 10 cm long x 0.8 cm thick piece of Douglas Fir. A timer was started. After 10 seconds, a second piece of Fir was bonded on its center point and at right angles to the first. Firm hand pressure was used to mate the surfaces. After a specified amount of time, a 4.5 kg tensile load was pneumatically applied to the 6.45 sq. cm bond area. The time at which the bond can support the 4.5 kg load was called the "4.5 kg tensile time". The results are reported in Table 8.

Table 8

Polyol, OH eq.	Ex. 110	Ex. 111	Ex. 112	Ex. 113
PHA	0.55	0.55	0.74	0.74
PEA	0.45	0.45	0.26	0.26
MDI eq.	2	1.8	2	1.8
Tert. Amine Catalyst	0.2	0.2	0.2	0.2
Visc.(cps)	7788	12700	6250	12050
Non-hairing	yes	yes	yes	yes
Phase sep. (%)	30	5	0	0
4.5 kg Tensile Time (minutes)	2-15	1.5-2.5	1	1

It can be seen from the data that with increasing % phase separation, 4.5 kg tensile time increases and is variable. This variability in the times given in Ex. 110 and 111 was due to the variation in the melt that is being extruded, that is the extrudate may be rich in the PHA, which has a rapid crystallization rate, one time and the following extrudate rich in PEA, which has a slower crystallization rate.

Claims

1. A non-hairing, moisture curable, hot melt composition having a number average molecular weight between 1,000 and 10,000 comprising the reaction product of two or more hydroxy-functional polymers with polyisocyanates wherein said hydroxy functional polymers are selected from:
   (1) linear polyester blends comprising a first and second polyester, wherein each polyester is the reaction product of a polyol and a polyacid, wherein

   $$a + b < \text{or} = 4, c + d > \text{or} = 6$$
   $$a + b > 4 \text{ and} \leq 6, c + d > \text{or} = 10$$
   $$a + b > 6 \text{ and} \leq 8, c + d > \text{or} = 12$$

   wherein a is the number of methylene moieties in the polyol used to form the first polyester,
   b is the number of methylene moieties in the polyacid used to form the first polyester,
   c is the number of methylene moieties in the polyol used to form the second polyester of the blend,
   d is the number of methylene moieties in the polyacid used to form the second polyester of the blend; and
   (2) a blend of at least one non-linear polyester and one linear polyester, wherein the non-linear polyester is selected from polyneopentyl adipate, polypropylene adipate and polycyclohexanedimethyl adipate, and the linear polyester is selected from polyethylene adipate, polybutylene succinate, and polyhexamethylene sebacate, provided that when the linear polyester is polyhexamethylene sebacate, the non-linear polyester is polyneopentyl adipate or polypropylene adipate; and
   (3) a blend of poly ϵ-caprolactone and at least one linear polyester selected from polyethylene adipate, polyethylene succinate and polybutylene succinate.

2. A non-hairing composition according to claim 1, wherein said hydroxy functional polymers are selected from group (1).

3. A non-hairing composition according to claim 1, wherein said hydroxy functional polymers are selected from group (2).

4. A non-hairing composition according to claim 1, wherein said hydroxy functional polymers are selected from group (3).

5. A non-hairing composition according to claim 1, wherein said hydroxy functional polymers are selected from
   (1) linear polyester blends, wherein the polyester is the reaction product of a diol and a diacid, wherein

$$a + b = 4, c + d > \text{or} = 6$$
$$a + b = 6, c + d > \text{or} = 10$$
$$a + b = 8, c + d > \text{or} = 12$$

wherein a is the number of methylene moieties in the diol used to form the first polyester,
b is the number of methylene moieties in the diacid used to form the first polyester,
c is the number of methylene moieties in the diol used to form the second polyester,
d is the number of methylene moieties in the diacid used to form the second polyester; and
(2) a blend of a linear and a non-linear polyester, wherein the non-linear polyester is selected from polyneopentyl adipate, polypropylene adipate and polycyclohexanedimethyl adipate, and the linear polyester is selected from polyethylene adipate, polybutylene succinate, and polyhexamethylene sebacate, provided that when the linear polyester is polyhexamethylene sebacate, the non-linear polyester is polyneopentyl adipate or polypropylene adipate;
(3) a mixture of polyethylene adipate and polyhexamethylene adipate; or
(4) a mixture of linear polyesters wherein one of the linear polyesters is poly ϵ-caprolactone and the others are selected from polyethylene adipate, polyethylene succinate and polybutylene succinate.

6. A non-hairing composition according to claim 5, wherein said hydroxy functional polymers are selected from group (1).

7. A non-hairing composition according to claim 5, wherein said hydroxy functional polymers are selected from group (2).

8. A non-hairing composition according to claim 5, wherein said hydroxy functional polymers are selected from group (3).

9. A non-hairing composition according to claim 5, wherein said hydroxy functional polymers are selected from group (4).

10. A non-hairing composition according to claim 8, wherein the weight ratio of polyethylene adipate to polyhexamethylene adipate is between 80:20 to 20: 80.

11. A non-hairing composition according to claim 10, wherein the weight ratio is between 70:30 and 30:70.

12. A non-hairing composition according to any preceding claim, wherein said polyisocyanates are aromatic polyisocyanates.

13. The hot melt composition according to any of claims 5 to 12, wherein said diol is selected from ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, dipropylene glycol, tripropylene glycol, 1,2-hexanediol, 1,4-butanediol, and 1,6-hexanediol.

14. A hot melt composition according to any preceding claim, wherein said polyisocyanates are selected from diphenylmethane-4,4'-diisocyanate, tolylene-2,4-diisocyanate, tolylene-2,6-diisocyanate, and mixtures thereof.

15. A hot melt composition according to claim 2 or any claim dependent on claim 2, wherein said polyacid is selected from saturated aliphatic dicarboxylic acids containing 4 to 10 carbon atoms, aromatic dicarboxylic acids containing 4 to 10 carbon atoms, aromatic dicarboxylic acids, and their corresponding esterified analogs.

16. A hot melt composition according to any preceding claim which contains a catalyst.

17. A hot melt composition according to claim 16 wherein said catalyst is selected from tertiary amines, metal-organic compounds, and co-curatives.

18. A hot melt composition according to claim 17, wherein the catalyst is dibutyltin dilaurate.

19. A hot melt composition according to claim 17, wherein the catalyst is a metal-organic compound and is present in an amount of at least 0.01 percent, based on the weight of the composition.

20. A method for bonding substrates which comprises contacting a substrate with a bond-forming amount of a hot melt moisture curable composition according to any preceding claim.

21. A composition according to any preceding claim, wherein the molecular weight of the hot melt composition is between 1000 and 6000.

22. A blend of hydroxy functional polymers comprising

(1) linear polyester blends, comprising a first and second polyester wherein each polyester is the reaction product of a polyol and a polyacid, wherein

$$a + b < \text{or} = 4, c + d > \text{or} = 6$$
$$a + b > 4 \text{ and} \leq 6, c + d > \text{or} = 10$$
$$a + b > 6 \text{ and} \leq 8, c + d > \text{or} = 12$$

wherein a is the number of methylene moieties in the polyol used to form the first polyester, b is the number of methylene moieties in the polyacid used to form the first polyester, c is the number of methylene moieties in the polyol used to form the second polyester of the blend, d is the number of methylene moieties in the polyacid used to form the second polyester of the blend; and

(2) a blend of at least one non-linear polyester and one linear polyester, wherein the non-linear polyester is selected from polyneopentyl adipate, polypropylene adipate and polycyclohexanedimethyl adipate, and the linear polyester is selected from polyethylene adipate, polybutylene succinate, and polyhexamethylene sebacate, provided that when the linear polyester is polyhexamethylene sebacate, the non-linear polyester is polyneopentyl adipate or polypropylene adipate; and

(3) a blend of poly ϵ-caprolactone and at least one linear polyester selected from polyethylene adipate, polyethylene succinate and polybutylene succinate.

23. A blend of hydroxy-functional polymers comprising

(1) linear polyester blends, wherein the polyester is the reaction product of a diol and a diacid, wherein

$$a + b = 4, c + d > \text{or} = 6$$
$$a + b = 6, c + d > \text{or} = 10$$
$$a + b = 8, c + d > \text{or} = 12$$

wherein a is the number of methylene moieties in the diol used to form the first polyester, b is the number of methylene moieties in the diacid used to form the first polyester, c is the number of methylene moieties in the diol used to form the second polyester, d is the number of methylene moieties in the diacid used to form the second polyester; and

(2) a blend of a linear and a non-linear polyester, wherein the non-linear polyester is selected from polyneopentyl adipate, polypropylene adipate and polycyclohexanedimethyl adipate, and the linear polyester is selected from polyethylene adipate, polybutylene succinate, and polyhexamethylene sebacate, provided that when the linear polyester is polyhexamethylene sebacate, the non-linear polyester is polyneopentyl adipate or polypropylene adipate;

(3) a mixture of polyethylene adipate and polyhexamethylene adipate; or

(4) a mixture of linear polyesters wherein one of the liner polyesters is poly ϵ-caprolactone and the others are selected from polyethylene adipate, polyethylene succinate and polybutylene succinate.

Patentansprüche

1. Nicht-fadenziehende, feuchthärtbare, Schmelzklebstoffzusammensetzung mit einer zahlengemittelten relativen Molekülmasse zwischen 1.000 und 10.000, umfassend das Reaktionsprodukt von zwei oder mehreren hydroxyfunktionellen Polymeren mit Polyisocyanaten, wobei die hydroxyfunktionellen Polymere ausgewählt werden aus:

(1) linearen Polyester-Blends, umfassend einen ersten und zweiten Polyester, wobei jeder Polyester das Reaktionsprodukt eines Polyols und einer Polysäure ist, worin sind:

$$a + b \leq 4, c + d \geq 6$$
$$a + b > 4 \text{ und } \leq 6, c + d \geq 10$$
$$a + b > 6 \text{ und } \leq 8, c + d \geq 12$$

darin sind:
a die zahl der Methylen-Teile in dem zur Bildung des ersten Polyesters verwendeten Polyol,
b die zahl der Methylen-Teile in der zur Bildung der ersten Polyesters verwendeten Polysäure,
c die zahl der Methylen-Teile in dem zur Bildung des zweiten Polyesters des Blends verwendeten Polyols,
d die zahl der Methylen-Teile in der zur Bildung des zweiten Polyesters des Blends verwendeten Polysäure; sowie
(2) einem Blend von mindestens einem nichtlinearen Polyester und einem linearen Polyester, wobei der nichtlineare Polyester, ausgewählt wird aus Polyneopentyladipat, Polypropylenadipat und Polycyclohexandimethyladipat, und der lineare Polyester, ausgewählt aus Polyethylenadipat, Polybutylensuccinat und Polyhexamethylensebacat, unter der Voraussetzung, daß, wenn der lineare Polyester Polyhexamethylensebacat ist, der nichtlineare Polyester Polyneopentyladipat oder Polypropylenadipat ist; sowie
(3) einem Blend von Poly-ϵ-caprolacton und mindestens einem linearen Polyester, ausgewählt aus Polyethylenadipat, Polyethylensuccinat und Polybutylensuccinat.

2. Nicht-fadenziehende Zusammensetzung nach Anspruch 1, bei welcher die hydroxyfunktionellen Polymere ausgewählt werden aus Gruppe (1).

3. Nicht-fadenziehende Zusammensetzung nach Anspruch 1, bei welcher die hydroxyfunktionellen Polymere ausgewählt werden aus Gruppe (2).

4. Nicht-fadenziehende Zusammensetzung nach Anspruch 1, bei welcher die hydroxyfunktionellen Polymere ausgewählt werden aus Gruppe (3).

5. Nicht-fadenziehende Zusammensetzung nach Anspruch 1, bei welcher die hydroxyfunktionellen Polymere ausgewählt werden aus:
(1) Linearen Polyester-Blends, umfassend einen ersten und zweiten Polyester, wobei jeder Polyester das Reaktionsprodukt eines Polyols und einer Polysäure ist, worin sind:

$$a + b = 4, c + d = 6$$
$$a + b = 6, c + d = 10$$
$$a + b = 8, c + d = 12$$

darin sind:
a die Zahl der Methylen-Teile in dem zur Bildung des ersten Polyesters verwendeten Polyol,
b die Zahl der Methylen-Teile in der zur Bildung der ersten Polyesters verwendeten Disäure,
c die Zahl der Methylen-Teile in dem zur Bildung des zweiten Polyesters des Blends verwendeten Diols,
d die Zahl der Methylen-Teile in der zur Bildung des zweiten Polyesters des Blends verwendeten Disäure; sowie
(2) einem Blend von mindestens einem nichtlinearen Polyester und einem linearen Polyester, wobei der nichtlineare Polyester ausgewählt wird aus Polyneopentyladipat, Polypropylenadipat und Polycyclohexandimethyladipat, und der lineare Polyester ausgewählt wird aus Polyethylenadipat, Polybutylensuccinat und Polyhexamethylensebacat, unter der Voraussetzung, daß, wenn der lineare Polyester Polyhexamethylensebacat ist, der nichtlineare Polyester Polyneopentyladipat oder Polypropylenadipat ist; sowie
(3) einer Mischung von Polyethylenadipat und Polyhexamethylenadipat; oder
(4) einer Mischung von linearen Polyestern, wobei einer der linearen Polyester Poly-ϵ-caprolacton ist und die anderen ausgewählt werden aus Polyethylenadipat, Polyethylensuccinat und Polybutylensuccinat.

6. Nicht-fadenziehende Zusammensetzung nach Anspruch 5, bei welcher die hydroxyfunktionellen Polymere ausgewählt werden aus Gruppe (1).

7. Nicht-fadenziehende Zusammensetzung nach Anspruch 5, bei welcher die hydroxyfunktionellen Polymere ausgewählt werden aus Gruppe (2).

8. Nicht-fadenziehende Zusammensetzung nach Anspruch 5, bei welcher die hydroxyfunktionellen Polymere ausgewählt werden aus Gruppe (3).

9. Nicht-fadenziehende Zusammensetzung nach Anspruch 5, bei welcher die hydroxyfunktionellen Polymere ausgewählt werden aus Gruppe (4).

10. Nicht-fadenziehende Zusammensetzung nach Anspruch 8, bei welcher das Gewichtsverhältnis von Polyethylenadipat zu Polyhexamethylenadipat 80:20 ... 20:80 beträgt.

11. Nicht-fadenziehende Zusammensetzung nach Anspruch 10, bei welcher das Gewichtsverhältnis 70:30 ... 30:70 beträgt.

12. Nicht-fadenziehende Zusammensetzung nach einem der vorgenannten Ansprüche, bei welcher die Polyisocyanate aromatische Polyisocyanate sind.

13. Schmelzklebstoffzusammensetzung nach Anspruch 5 bis 12, bei welcher das Diol ausgewählt wird aus: Ethylenglykol, Diethylenglykol, Triethylenglykol, 1,2-Propylenglykol, Dipropylenglykol, Tripropylenglykol, 1,2-Hexandiol, 1,4-Butandiol und 1,6-Hexandiol.

14. Schmelzklebstoffzusammensetzung nach einem der vorgenannten Ansprüche, bei welcher die Polyisocyanate ausgewählt werden aus: Diphenylmethan-4,4'-diisocyanat, Tolylen-2,4-diiosocyanat, Tolylen-2,6-diisocyanat und deren Mischungen.

15. Schmelzklebstoffzusammensetzung nach Anspruch 2 oder einem von Anspruch 2 abhängigen Anspruch, bei welcher die Polysäure ausgewählt wird aus: gesättigten aliphatischen Dicarbonsäuren mit 4 bis 10 Kohlenstoffatomen, aromatischen Dicarbonsäuren mit 4 bis 10 Kohlenstoffatomen, aromatischen Dicarbonsäuren und ihren entsprechenden veresterten analogen Vertretern.

16. Schmelzklebstoffzusammensetzung nach einem der vorgenannten Ansprüche, die einen Katalysator enthält.

17. Schmelzklebstoffzusammensetzung nach Anspruch 16, bei welcher der Katalysator ausgewählt wird aus *tert*-Aminen, metallorganischen Verbindungen und Co-Härtungsmitteln.

18. Schmelzklebstoffzusammensetzung nach Anspruch 17, bei welcher der Katalysator Dibutylzinn-dilaurat ist.

19. Schmelzklebstoffzusammensetzung nach Anspruch 17, bei welcher der Katalysator eine metallorganische Verbindung ist und in einer Menge von mindestens 0,01 % bezogen auf das Gewicht der Zusammensetzung vorliegt.

20. Verfahren zum Verkleben von Substraten, welches Verfahren umfaßt: Kontaktieren eines Substrats mit einer eine Verklebung bildenden Menge eines feuchthärtbaren Schmelzklebstoffs nach einem der vorgenannten Ansprüche.

21. Zusammensetzung nach einem der vorgenannten Ansprüche, bei welcher die relative Molekülmasse der Schmelzklebstoffzusammensetzung zwischen 1.000 und 6.000 beträgt.

22. Blend von hydroxyfunktionellen Polymeren, umfassend:
(1) Lineare Polyester-Blends, umfassend einen ersten und zweiten Polyester, wobei jeder Polyester das Reaktionsprodukt eines Polyols und einer Polysäure ist, worin sind:

$$a + b \leq 4, c + d \geq 6$$
$$a + b > 4 \text{ und } \leq 6, c + d \geq 10$$
$$a + b > 6 \text{ und } \leq 8, c + d \geq 12$$

darin sind:

a die Zahl der Methylen-Teile in dem zur Bildung des ersten Polyesters verwendeten Polyol,
b die Zahl der Methylen-Teile in der zur Bildung der ersten Polyesters verwendeten Polysäure,
c die Zahl der Methylen-Teile in dem zur Bildung des zweiten Polyesters des Blends verwendeten Polyols,
d die Zahl der Methylen-Teile in der zur Bildung des zweiten Polyesters des Blends verwendeten Polysäure; sowie

(2) ein Blend von mindestens einem nichtlinearen Polyester und einem linearen Polyester, wobei der nichtlineare Polyester ausgewählt wird aus Polyneopentyladipat, Polypropylenadipat und Polycyclohexandimethyladipat, und der lineare Polyester ausgewählt wird aus Polyethylenadipat, Polybutylensuccinat und Polyhexamethylensebacat, unter der Voraussetzung, daß, wenn der lineare Polyester Polyhexamethylensebacat ist, der nichtlineare Polyester Polyneopentyladipat oder Polypropylenadipat ist; sowie

(3) ein Blend von Poly-ϵ-caprolacton und mindestens einem linearen Polyester, ausgewählt aus Polyethylenadipat, Polyethylensuccinat und Polybutylensuccinat.

23. Blend von hydroxyfunktionellen Polymeren, umfassend:

(1) Lineare Polyester-Blends, umfassend einen ersten und zweiten Polyester, wobei jeder Polyester das Reaktionsprodukt eines Polyols und einer Polysäure ist, worin sind:

$$a + b = 4, c + d = 6$$
$$a + b = 6, c + d = 10$$
$$a + b = 8, c + d = 12$$

darin sind:

a die Zahl der Methylen-Teile in dem zur Bildung des ersten Polyesters verwendeten Polyol,
b die Zahl der Methylen-Teile in der zur Bildung der ersten Polyesters verwendeten Disäure,
c die Zahl der Methylen-Teile in dem zur Bildung des zweiten Polyesters des Blends verwendeten Diols,
d die Zahl der Methylen-Teile in der zur Bildung des zweiten Polyesters des Blends verwendeten Disäure; sowie

(2) ein Blend von mindestens einem nichtlinearen Polyester und einem linearen Polyester, wobei der nichtlineare Polyester ausgewählt wird aus Polyneopentyladipat, Polypropylenadipat und Polycyclohexandimethyladipat, und der lineare Polyester ausgewählt wird aus Polyethylenadipat, Polybutylensuccinat und Polyhexamethylensebacat, unter der Voraussetzung, daß, wenn der lineare Polyester Polyhexamethylensebacat ist, der nichtlineare Polyester Polyneopentyladipat oder Polypropylenadipat ist; sowie

(3) eine Mischung von Polyethylenadipat und Polyhexamethylenadipat; oder

(4) eine Mischung von linearen Polyestern, wobei einer der linearen Polyester Poly-ϵ-caprolacton ist und die anderen ausgewählt werden aus Polyethylenadipat, Polyethylensuccinat und Polybutylensuccinat.

Revendications

1. Composition thermofusible durcissable à l'humidité, non-filante, ayant un poids moléculaire moyen en nombre compris entre 1 000 et 10 000, comprenant le produit de reaction de deux ou plusieurs polymères à fonction hydroxy avec des polyisocyanates, où lesdits polymères à fonction hydroxy sont choisi parmi :

(1) les mélanges de polyesters linéaires comprenant un premier et un second polyester, où chaque polyester est le produit de réaction d'un polyol et d'un polyacide, où

$$a + b < \text{ou} = 4, c + d > \text{ou} = 6$$
$$a + b > 4 \text{ et } \leq 6, c + d > \text{ou} = 10$$
$$a + b > 6 \text{ et } \leq 8, c + d > \text{ou} = 12$$

où a est le nombre de parties méthylène dans le polyol utilisé pour former le premier polyester,
b est le nombre de parties méthylène dans le polyacide utilisé pour former le premier polyester,
c est le nombre de parties méthylène dans le polyol utilisé pour former le second polyester du mélange,
d est le nombre de parties méthylène dans le polyacide utilisé pour former le second polyester du mélange; et
(2) un mélange d'au moins un polyester nonlinéaire et d'un polyester linéaire, où le polyester linéaire est choisi parmi l'adipate de polynéopentyle, l'adipate de polypropylène, et l'adipate de polycyclohexanediméthyle, et le polyester linéaire est choisi parmi l'adipate de polyéthylène, le succinate de polybutylène, et le sébacate de polyhexaméthylène, à condition que lorsque le polyester linéaire est le sébacate de polyhexaméthylène, le polyester nonlinéaire est l'adipate de polynéopentyle ou l'adipate de polypropylène ; et
(3) un mélange de poly ϵ-caprolactone et d'au moins un polyester linéaire choisi parmi l'adipate de polyéthylène, le succinate de polyéthylène et le succinate de polybutylène.

2. Composition non-filante selon la revendication 1, dans laquelle lesdits polymères à fonction hydroxy sont choisis dans le groupe (1).

3. Composition non-filante selon la revendication 1, dans laquelle lesdits polymères à fonction hydroxy sont choisis dans le groupe (2).

4. Composition non-filante selon la revendication 1, dans lesquels lesdits polymères à fonction hydroxy sont choisis dans le groupe (3).

5. Composition non-filante selon la revendication 1, dans laquelle lesdits polymères à fonction hydroxy sont choisis parmi
(1) des mélanges de polyester linéaire, où le polyester est le produit de réaction d'un diol et d'un diacide, où

$$a + b = 4, c + d > \text{ou} = 6$$
$$a + b = 6, c + d > \text{ou} = 10$$
$$a + b = 8, c + d > \text{ou} = 12$$

où a est le nombre de parties méthylène dans le diol utilisé pour former le premier polyester,
b est le nombre de parties méthylène dans le diacide utilisé pour former le premier polyester,
c est le nombre de parties méthylène dans le diol utilisé pour former le second polyester,
d est le nombre de parties méthylène dans le diacide utilisé pour former le second polyester ; et
(2) un mélange d'un polyester linéaire et d'un polyester non-linéaire, où le polyester non-linéaire est choisi parmi l'adipate de polynéopentyle, l'adipate de polypropylène, et l'adipate de polycyclohexanediméthyle, et le polyester linéaire est choisi parmi l'adipate de polyéthylène, le succinate de polybutylène, et le sébacate de polyhexaméthylène, à condition que lorsque le polyester linéaire est le sébacate de polyhexaméthylène, le polyester nonlinéaire est l'adipate de polynéopentyle ou l'adipate de polypropylène ;
(3) un mélange d'adipate de polyéthylène et d'adipate de polyhexaméthylène ; ou
(4) un mélange de polyesters linéaires où l'un des polyesters linéaires est la poly ϵ-caprolactone et les autres sont choisis parmi l'adipate de polyéthylène, le succinate de polyéthylène et le succinate de polybutylène.

6. Composition non-filante selon la revendication 5, dans laquelle lesdits polymères à fonction hydroxy sont choisis dans le groupe (1)

7. Composition non-filante selon la revendication 5, dans laquelle lesdits polymères à fonction hydroxy sont choisis dans le groupe (2).

8. Composition non-filante selon la revendication 5, dans laquelle lesdits polymères à fonction hydroxy sont choisis dans le groupe (3).

9. Composition non-filante selon la revendication 5, dans laquelle lesdits polymères à fonction hydroxy sont choisis dans le groupe (4).

10. Composition non-filante selon la revendication 8, dans laquelle le rapport pondéral de l'adipate de polyéthylène à l'adipate de polyhexaméthylène est compris entre 80:20 et 20:80.

11. Composition non-filante selon la revendication 10, dans laquelle le rapport pondéral est compris entre 70:30 et 30:70.

12. Composition non-filante selon l'une quelconque des revendications précédentes, dans laquelle lesdits polyisocyanates sont des polyisocyanates aromatiques.

13. Composition thermofusible selon l'une quelconque des revendications 5 à 12, dans laquelle ledit diol est choisi parmi l'éthylène glycol, le diéthylène glycol, le triéthylène glycol, le 1,2-propylène glycol, le dipropylène glycol, le tripropylène glycol, le 1,2-hexanediol, le 1,4-butanediol, et le 1,6-hexanediol.

14. Composition thermofusible selon l'une quelconque des revendications précédentes, dans laquelle lesdits polyisocyanates sont choisis parmi le diphénylméthane-4,4'-diisocyanate, le tolylène-2,4-diisocyanate, le tolylène-2,6-diisocyanate, et leurs mélanges.

15. Composition thermofusible selon la revendication 2 ou une revendication quelconque dépendant de la revendication 2, dans laquelle ledit polyacide est choisi parmi les acides dicarboxyliques aliphatiques saturés contenant de 4 à 10 atomes de carbone, les acides dicarboxyliques aromatiques contenant de 4 à 10 atomes de carbone, les acides dicarboxyliques aromatiques, et leurs analogues estérifiés correspondants.

16. Composition thermofusible selon l'une quelconque des revendications précédentes, qui comprend un catalyseur.

17. Composition thermofusible selon la revendication 16, dans laquelle ledit catalyseur est choisi parmi les amines tertiaires, les composés organo-métalliques et les agents de co-durcissement.

18. Composition thermofusible selon la revendication 17, dans laquelle le catalyseur est le dilaurate de dibutylétain.

19. Composition thermofusible selon la revendication 17, dans laquelle le catalyseur est un composé organo-métallique et est présent en une quantité d'au moins 0,01 pour cent, sur la base du poids de la composition.

20. Procédé pour lier des substrats qui comprend la mise en contact d'un substrat avec une quantité formant liaison d'une composition durcissable à l'humidité thermofusible selon l'une quelconque des revendications précédentes.

21. Composition selon l'une quelconque des revendications précédentes, dans laquelle le poids moléculaire de la composition thermofusible est compris entre 1 000 et 6 000.

22. Mélange de polymères à fonction hydroxy comprenant

(1) des mélanges de polyester linéaire, comprenant un premier et un second polyester où chaque polyester est le produit de réaction d'un polyol et d'un polyacide, où

$$a + b < \text{ou} = 4, c + d > \text{ou} = 6$$
$$a + b > 4 \text{ et} \leq 6, c + d > \text{ou} = 10$$
$$a + b > 6 \text{ et} \leq 8, c + d > \text{ou} = 12$$

où a est le nombre de parties méthylène dans le polyol utilisé pour former le premier polyester, b est le nombre de parties méthylène dans le polyacide utilisé pour former le premier polyester, c est le nombre de parties méthylène dans le polyol utilisé pour former le second polyester du mélange, d est le nombre de parties méthylène dans le polyacide utilisé pour former le second polyester du

mélange; et

(2) un mélange d'au moins un polyester nonlinéaire et d'un polyester linéaire, où le polyester non-linéaire est choisi parmi l'adipate de polynéopentyle, l'adipate de polypropylène, et l'adipate de polycyclohexanediméthyle, et le polyester linéaire est choisi parmi l'adipate de polyéthylène, le succinate de polybutylène, et le sébacate de polyhexaméthylène, à condition que lorsque le polyester linéaire est le sébacate de polyhexaméthylène, le polyester non-linéaire est l'adipate de polynéopentyle ou l'adipate de polypropylène ; et

(3) un mélange d'adipate de poly ϵ-caprolactone et d'au moins un polyester linéaire choisi parmi l'adipate de polyéthylène, le succinate de polyéthylène et le succinate de polybutylène.

23. Mélange de polymères à fonction hydroxy comprenant

(1) des mélanges de polyester linéaire, où le polyester est le produit de réaction d'un diol et d'un diacide, où

$$a + b = 4, c + d > \text{ou} = 6$$
$$a + b = 6, c + d > \text{ou} = 10$$
$$a + b = 8, c + d > \text{ou} = 12$$

où a est le nombre de parties méthylène dans le diol utilisé pour former le premier polyester, b est le nombre de parties méthylène dans le diacide utilisé pour former le premier polyester, c est le nombre de parties méthylène dans le diol utilisé pour former le second polyester, d est le nombre de parties méthylène dans le diacide utilisé pour former le second polyester ; et

(2) un mélange d'un polyester linéaire et d'un polyester non-linéaire, où le polyester non-linéaire est choisi parmi l'adipate de polynéopentyle, l'adipate de polypropylène, et l'adipate de polycyclohexanediméthyle, et le polyester linéaire est choisi parmi l'adipate de polyéthylène, le succinate de polybutylène, et le sébacate de polyhexaméthylène, à condition que lorsque le polyester linéaire est le sébacate de polyhexaméthylène, le polyester nonlinéaire est l'adipate de polynéopentyle ou l'adipate de polypropylène ;

(3) un mélange d'adipate de polyéthylène et d'adipate de polyhexaméthylène ; ou

(4) un mélange de polyesters linéaires où l'un des polyesters linéaires est la poly ϵ-caprolactone et les autres sont choisis parmi l'adipate de polyéthylène, le succinate de polyéthylène et le succinate de polybutylène.